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FOR ION- POLAR-MOLECULE COLLISIONS
INVOLVING METHYL CYANIDE**

by

John V. Dugan, Jr., and James H. Rice
Lewis Research Center

and

John L. Magee
University of Notre Dame

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By John V. Dugan, Jr., and James H. Rice

Lewis Research Center
Cleveland, Ohio

John L. Magee

University of Notre Dame
Notre Dame, Indiana

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ABSTRACT

The cross sections (CS) for capture collisions between the symmetric top molecule CH_3CN and molecular ions are calculated numerically. These ion-molecule collisions have been studied experimentally and have large reaction CS, Q_R . Calculations are done to study the role of the added degree of rotational freedom by comparing capture CS for tops with linear molecules. The monoenergetic CS $\sigma_c(\epsilon_1)$ (where ϵ_1 is the ion energy and T_R is the top rotational temperature) are less than the maximum classical CS σ_{max} , but much larger than Langevin CS σ_L . The integrated σ_c , Q_c , agree well with Q_R for the collisions studied. The σ_c values for CH_3CN are nearly independent of target geometry.

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CALCULATION OF CAPTURE CROSS SECTIONS FOR ION-POLAR-MOLECULE COLLISIONS INVOLVING METHYL CYANIDE*

by John V. Dugan, Jr., James H. Rice, and John L. Magee†

Lewis Research Center

SUMMARY

The cross sections for capture collisions between the symmetric top molecule methyl cyanide (CH_3CN) and several molecular ions are calculated by a numerical approach previously used to study collisions between ions and linear polar molecules. These ion-molecule collisions involving CH_3CN have been studied in the mass spectrometer and have large experimental reaction cross sections. Calculations are also done for symmetric tops with varying moments of inertia about their symmetry axes. This was done to study the role of the added degree of rotational freedom by comparing symmetric top capture cross sections with those for linear molecules. The mono-energetic cross sections σ_c obtained in this report (for tops at rotational temperature T_R) are less than the maximum classical cross section σ_{max} which is assumed by the experimentalists. These σ_c values are much larger than Langevin cross sections σ_L and have a slope $\epsilon_1^{-0.65}$ where ϵ_1 is the ion energy. The integrated values of σ_c (macroscopic cross section Q_c) are within 50 percent of the reaction cross sections for the collisions of CH_3CN^+ and $\text{C}_6\text{D}_{12}^+$ with CH_3CN . The cross sections for different symmetric tops are nearly equal to the linear molecule results so that σ_c appears independent of molecular geometry of the target species.

INTRODUCTION

The capture cross sections for collisions between ions and polar molecules have been

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† Professor of Chemistry, University of Notre Dame.

studied by numerical methods in references 1 to 3. In reference 1 the species studied were hypothetical linear and symmetric top molecules. The accuracy of the numerical integration technique was checked with the conservation of energy equation. An automatic step-size changing routine was used to calculate the capture cross section for the $\text{HCl}^+ + \text{HCl}$ collision in reference 3. The numerical results (plotted against relative translational energy) showed the same slope as an approximate theory predicts, but the absolute values differed by about 40 percent. The ion-molecule (IM) trajectories were studied under time reversal to ensure correct solutions of the differential equations. The rotational motion of linear HCl was followed in such a way as to avoid numerical singularities that arise from retaining only two coordinates in any integration step (ref. 3).

Certain ion-symmetric top (polar) molecule reaction cross sections have been studied in the mass spectrometer as reported in references 4 and 5. These reaction cross sections can be related to the capture cross sections by reaction efficiencies. The methyl cyanide molecule (CH_3CN) is a polar target species which was particularly well studied in reference 5. The purpose of this paper is to calculate numerical capture cross sections for certain IM collisions involving the CH_3CN molecule.

It also includes a description of the variable step-size approach, used both in this study and in reference 3, with details of its application. The cross sections σ_c are given as functions of ion translational energy ϵ_1 for a distribution of targets at rotational temperature T_R . Integrated values of σ_c will be compared with experimental data, although the comparison is somewhat qualified. The computer approach employs the integration routine of reference 3 with a special Euler angle transformation. This coordinate transformation ensures accurate solutions for the symmetric top rotational motion.

DETAILS OF CALCULATION

Numerical Approach

The Lagrangian equations of motion were solved for the ion-molecule (IM) collision with an interaction potential composed of the classical ion-permanent dipole and ion-induced dipole (electronic polarizability terms). All collisions studied involved CH_3CN , which was represented as a spherically polarizable ideal permanent dipole target interacting with point-charge ions. The molecule rotates as the IM pair move relative to each other translationally. These equations and the values of molecular constants are included in appendix A and table I. The coordinate system used for the collision model is shown in figure 1. The numerical singularity difficulties (whose avoidance requires

TABLE I. - MOLECULAR CONSTANTS

[Dipole moment, 3.92 DU (1.31×10^{-29} (C)(m)); electronic polarizability, $3.8 \cdot \text{\AA}^3$ ($3.8 \times 10^{-30} \text{ m}^3$); moment of inertia, I_1 , 9.12×10^{-46} (kg)(m²) for all cases.]

Case	Reduced mass, m, kg	Moment of inertia, I_2 , (kg)(m ²)
I	3.41×10^{-26}	5.47×10^{-47}
II	4.78	5.47×10^{-47}
III	3.41	2.19×10^{-46}
IV	3.41	0

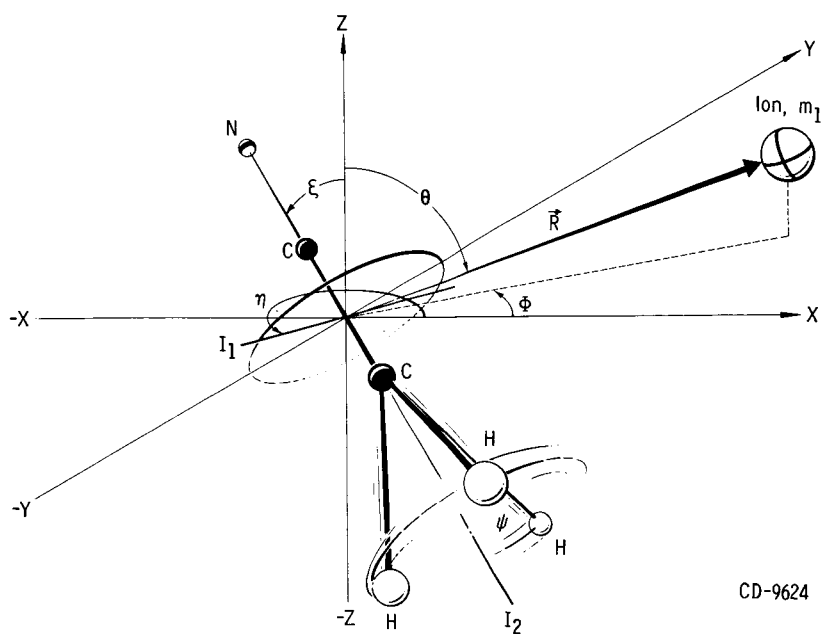


Figure 1. - Coordinate system employed in computer study of interaction between ion and symmetric top polar molecule methyl cyanide.

the coordinate transformation) are caused by the $\sin \xi$ term in the denominator of equation (A7). This term prevents accurate calculation of the azimuthal acceleration $\ddot{\eta}$. The singularity is avoided by transforming to a second Euler angle system whose z-axis is orthogonal to that of the first system. The details of this transformation have been given in reference 6. The transformation was made whenever the rotating top entered "polar caps" within 30° of either the positive or negative z axis (in either coordinate system).

The integration procedure and step-size changing routine are based on the relative error encountered in conservation of energy. These are described in appendix B. A total error (in energy) in the range 10^{-2} to 10^{-3} was generally sufficient to assure satisfactory behavior of coordinates and derivatives under time reversal. When energy conservation was violated even with small step size (low-ion velocity, small-impact parameter) the order of the integration routine was changed to solve the trajectory satisfactorily.

Experimental Reaction Cross Sections

Experimental reaction cross sections for ion-polar molecule systems have been obtained from self-consistent fits of cross section against ion energy in reference 5. It is assumed in that study that the collision pairs have variable reaction efficiencies. It should be noted that the present computer calculation takes no account of such reaction efficiencies (which are called transmission coefficients in ref. 5). The capture cross section is simply a numerical upper limit to the reaction cross section Q_R (see eq. (9) of ref. 5). The classical upper limit to the capture cross section has been discussed previously in references 2 to 6.

It should be noted that reactions can occur at any value of ion energies from a thermal lower limit to the maximum energy (set by the applied repeller voltage in the experiment). Thus the corresponding numerical cross section of interest is an integrated value of the microscopic cross section as a function of ion energy. These integrated cross sections will be compared with experimental cross-section results. However, the manner of interpretation of results is limited because the numerical calculation takes no account of reaction efficiencies. This comparison is further complicated because the approximate form of the capture cross section adopted in reference 5 is not valid at low ion energies as will be discussed later.

Initial Conditions

The initial conditions for the dipole rotator were generated from a distribution at $T_R = 500$ K because experiments were done at this temperature. Three to five sets of 36 and/or 54 trajectories were used to generate each point on the C_R against b^2 curve. This was done for initial ion velocities of 5.5×10^4 , 10^5 , and 2×10^5 centimeters per second. Values of reduced mass $m = m_1 m_2 / (m_1 + m_2)$ (where m_1 is the ion mass and m_2 is the mass of the polar molecule) correspond to the $\text{CH}_3\text{CN} + \text{CH}_3\text{CN}^+$ and $\text{CH}_3\text{CN} + \text{C}_6\text{D}_{12}^+$ collision pairs. The ion energies corresponding to the velocities studied range from several hundredths of an electron volt (eV) to several eV. The IM reactions of interest have been studied experimentally from ion energies $\sim kT_R$ up to several eV.

Four different collision pairs were studied. The first two systems consisted of CH_3CN colliding with (I) CH_3CN^+ (the "parent" ion) and (II) with $\text{C}_6\text{D}_{12}^+$. Case III consisted of a pseudo CH_3CN molecule with a moment of inertia about the symmetry axis I_2 equal to four times that of the value for CH_3CN . The limit where I_2 goes to zero was studied in case IV. This system consisted of a linear polar target with the same polarizability and dipole moment as CH_3CN . The reduced mass assigned to the pairs in cases III and IV was the same as for the CH_3CN molecule and ion (case I).

Numerical Capture Cross Section

Because the probability of capture is not a simple function of impact parameter, the numerical capture cross section σ_c must be defined in terms of a collision ratio C_R as in references 1 and 3. This collision ratio is the fraction of IM trajectories in which the ion and molecule approach within 2 \AA (0.2 nm). The choice of 2 \AA as the cut-off distance r_c appears arbitrary, but in the present calculation it has been found that σ_c is insensitive to r_c as long as the r_c value is not made too large. This limit on r_c is $\leq 4 \text{ \AA}$ (≤ 0.4 nm) at low ion velocity and less than 3 \AA (0.3 nm) at high ion velocity. These r_c values correspond to the range of van der Waals radii and hard-core cross sections reported for the molecules of interest in reference 5.

The numerical cross section as a function of the free-particle impact parameter b is given by

$$\sigma_c \equiv \pi b_c^2 = \pi \int_0^\infty C_R(b) d(b^2) \quad (1)$$

that is, simply π times the area under the curve C_R against b^2 . For comparison

with experiment one requires the integrated numerical cross section (see eq. (5) of ref. 5).

$$Q_c = \frac{1}{\epsilon_m} \int_{\epsilon_i}^{\epsilon_m} \sigma_c(\epsilon_1) d\epsilon_1 \quad (2)$$

In equation (2), ϵ_m is the maximum ion energy (fixed by the repeller voltage), and ϵ_i is the minimum ion energy (taken as thermal).

The maximum classical cross section for capture has the following form as mentioned in references 1 to 5.

$$\sigma_{\max} = \frac{\pi \mu e}{\epsilon} + \sigma_L = \sigma_D + \sigma_L \quad (3)$$

where ϵ is the relative translational energy of the IM pair and σ_L is the familiar Langevin cross section which is equal to $\pi(2\alpha e^2/\epsilon)^{1/2}$. The experimentalists have adopted this form of the cross section to obtain reaction efficiencies from their data. The relative translational energy is related to the ion energy for a fixed velocity by $\epsilon = (m/m_1)\epsilon_1$. Thus σ_{\max} can be rewritten as

$$\sigma_{\max}(\epsilon_1) = \left(\frac{m_1}{m}\right) \sigma'_D(\epsilon_1) + \sqrt{\frac{m_1}{m}} \sigma'_L(\epsilon_1) \quad (4)$$

where $\sigma'_D(\epsilon_1) = \pi \mu e / \epsilon_1$ and $\sigma'_L(\epsilon_1) = \pi(2\alpha e^2 / \epsilon_1)^{1/2}$. It is assumed that the ion velocity is much greater than the neutral velocity; this introduces some slight error for energies near ϵ_i . Also, it will later be pointed out that the term containing ϵ_i is not negligible in the σ_L contribution to the integrated cross section Q_{\max} .

RESULTS AND DISCUSSION

Case I: $\text{CH}_3\text{CN}^+ + \text{CH}_3\text{CN}$ Collision

Curves of collision ratio C_R against impact parameter b for the CH_3CN -parent ion collision are given in figure 2 for ion velocities of 5.5×10^4 , 10^5 , and 2×10^5 centimeters per second. The variations in C_R with specified total error and random number sets (36 or 54 trajectories) are shown by the range-of-error bars. The $v = 5.5 \times 10^4$ value corresponds to an ion energy of only 0.064 eV. The somewhat irregular curve in

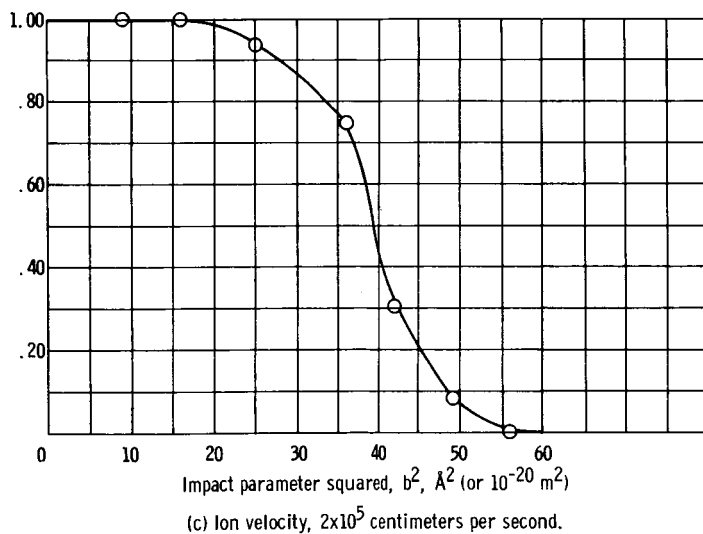
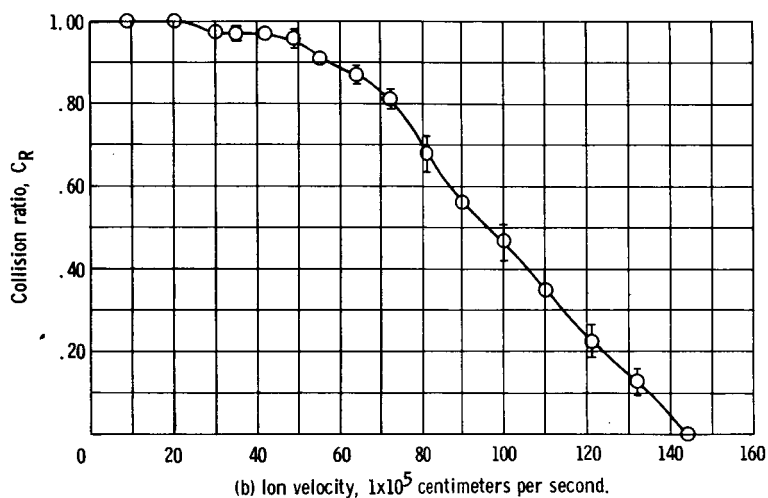
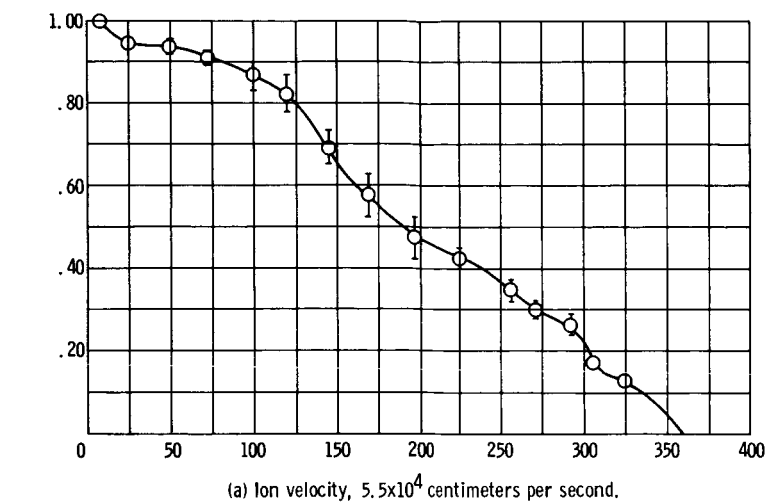


Figure 2. - Variation of collision ratio with free-particle impact parameter for rotational temperature of 500 K. Methyl cyanide parent-ion collision; dipole moment, 3.92 Debye Units (1.31×10^{-29} C(m)); electronic polarizability, 3.8 \AA^3 ($3.8 \times 10^{-30} \text{ m}^3$). Total error, 5×10^{-3} and 1×10^{-2} ; 3 To 5 random number sets per point.

figure 2(a) is characteristic of the low velocity behavior observed in references 1 and 3. The C_R curve becomes smoother at $v = 10^5$, and the structure disappears entirely for high velocity. For $v = 2 \times 10^5$ centimeters per second the C_R values drop off to zero rapidly at b values beyond 6 \AA (0.6 nm).

The σ_c values are plotted against initial ion energy in figure 3 and compared with values of the Langevin σ_L , permanent dipole σ_D and σ_{\max} cross sections. The ion energy is equal to twice the relative translational energy for this case. The σ_c values have a slope $\cong \epsilon_1^{-0.66}$, that is, somewhat steeper than the calculated $\epsilon^{-1/2}$ for the

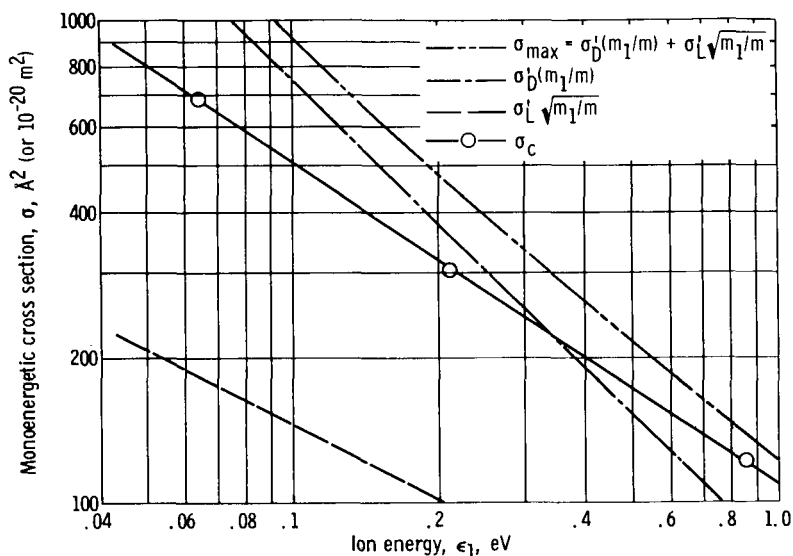


Figure 3. - Comparison of numerically calculated capture cross section with various classical cross sections for methyl cyanide parent-ion collision.

HCl + HCl⁺ system in reference 3. The symmetric top σ_c values are, however, much larger than the Langevin (simple polarizability) theory predicts.

The integrated values of σ_c (over all possible relative energies), designated as Q_c , are obtained from equation (2).

The corresponding capture cross section assumed by the experimentalists is the integrated form of equation (4):

$$Q_{\max} = \frac{1}{\epsilon_m} \int_{\epsilon_i}^{\epsilon_m} \sigma_{\max}(\epsilon_1) d\epsilon_1 = \frac{\pi \mu e}{\epsilon_m} \ln \left(\frac{\epsilon_m}{\epsilon_i} \right) + \frac{2\pi(2\alpha e^2)^{1/2}}{\epsilon_m} \left(\sqrt{\epsilon_m} - \sqrt{\epsilon_i} \right) \quad (5)$$

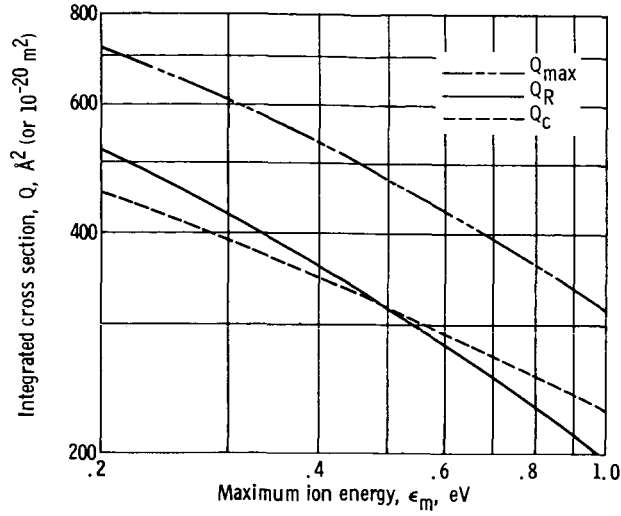


Figure 4. - Comparison of integrated numerical capture cross section Q_c with experimentally assumed capture cross section Q_{max} and observed reaction cross section Q_R for methyl cyanide parent-ion collision.

The integrated numerical cross section, obtained by assuming that σ_c varies as the n^{th} power of the ion energy, is

$$Q_c = \frac{1}{\epsilon_m} \int_{\epsilon_i}^{\epsilon_m} \sigma_c(\epsilon_1) d\epsilon_1 = \frac{\sigma_{co}}{\epsilon_m} \frac{(\epsilon_m^{1-n} - \epsilon_i^{1-n})}{(1-n)} \quad (6)$$

where σ_{co} is a constant obtained from the assumed $\sigma_{co} \epsilon^{-n}$ dependence of the mono-energetic cross section. It should be noted that, for $m < m_1$ (in all cases), the experimental values of ion energy will correspond to smaller values of relative energy. The numerical predictions have a slope nearly $\epsilon_m^{-0.5}$. The experimentally observed reaction cross section is plotted for comparison with Q_c and Q_{max} in figure 4. It should be noted that the term containing $\epsilon_i^{1/2}$ has been retained in computing Q_c and Q_{max} but was not retained in the form of Q_R derived in reference 5. An effective reaction efficiency P_D of 0.72 was assumed with the form of σ_{max} in reference 5 to obtain Q_R ; this precludes any simple interpretation of the disparity in results. Figure 5 shows σ_c as a function of ion energy ϵ_1 for the $\text{CH}_3\text{CN} + \text{C}_6\text{D}_{12}^+$ collision. The inverse dependence on ion velocity for fixed reduced mass is identical to the results for the CH_3CN parent ion collision shown in figure 3. Comparison of figures 3 and 5 indicates that σ_c depends only on ion energy. From this fact one can infer that σ_c depends roughly inversely on the mass for constant velocity v .

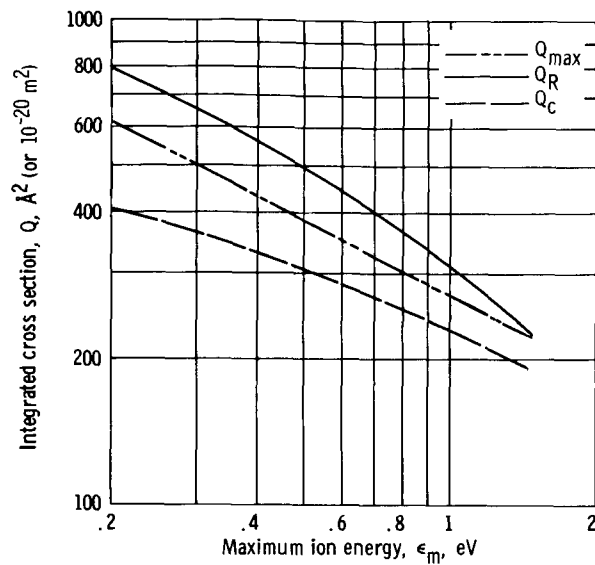


Figure 6. - Comparison of integrated numerical capture cross section Q_C with experimentally assumed capture cross section Q_{max} and observed reaction Q_R for collision of methyl cyanide with $C_6D_{12}^+$.

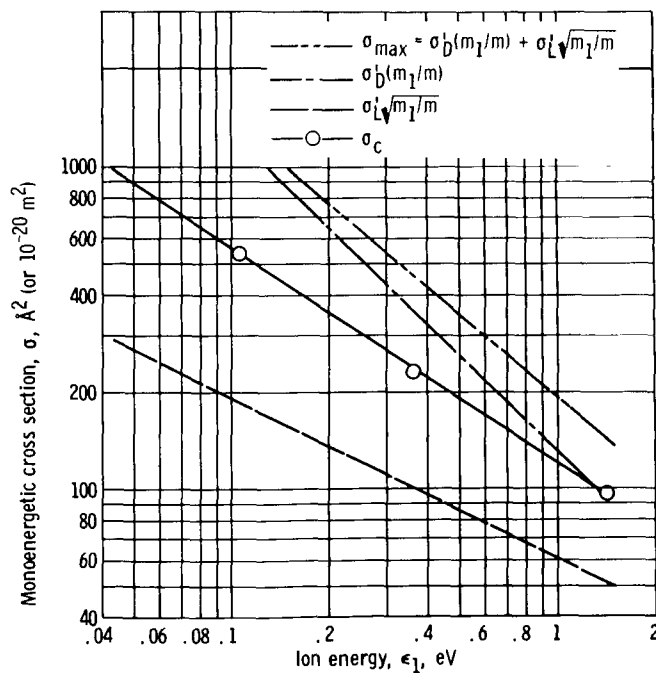


Figure 5. - Comparison of numerically calculated capture cross section with various classical cross sections for collision of methyl cyanide with $C_6D_{12}^+$.

Case II: $C_6D_{12}^+ + CH_3CN$

As a result of the two dependences on v and m , the σ_c values appear nearly independent of ion for the range of ion energies studied with CH_3CN targets. This system was studied at the same ion velocities as case I, so the numerical points are merely shifted to higher ϵ_1 because m_1 is larger. The experimental reaction cross section Q_R is plotted for comparison in figure 6. An effective reaction efficiency of 0.67 was assumed in reference 5. Unlike the parent ion reaction, the values of Q_R are greater than Q_c and Q_{max} at all energies.

Case III: Pseudo $CH_3CN^+ + CH_3CN$ Collision

The value of I_2/I_1 chosen was 0.24; all other constants were the same as for the case I. There were no significant differences in the C_R curves between cases I and III. This indicates that the interaction is insensitive to the value of moment of inertia about

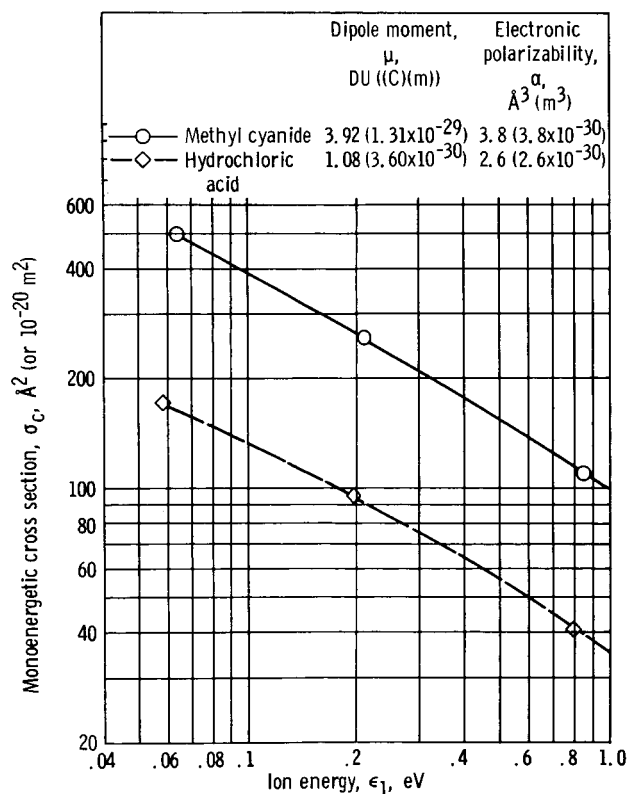


Figure 7. - Comparison of monoenergetic capture cross section results for linear methyl cyanide ($CH_3CN + CH_3CN^+$) collision with results for hydrochloric acid.

the symmetry axis for symmetric tops. The corresponding cross section values σ_c and Q_c do not differ from the case I results.

Case IV: CH_3CN^+ + "Linear CH_3CN "

This hypothetical linear molecule target was studied to investigate the parent ion collision in the limit where the rotational degree of freedom about the symmetry axis vanishes. The C_R against b^2 curves differ only slightly from those of cases I and III at low velocity. However, there is a difference (of several percent) between σ_c values in this region. The results are shown in figure 7 and are compared with similar results for the linear HCl (ref. 3). The HCl results have a smaller dipole moment and polarizability than CH_3CN ; $\alpha = 2.6 \text{ \AA}^3$ ($2.6 \times 10^{-30} \text{ m}^3$), $\mu = 1.08 \text{ D. U.}$ ($3.60 \times 10^{-30} \text{ (C)(m)}$). The results indicate that the cross section does have the dipole moment dependence that the approximate theory predicts (refs. 1 to 3). The theory predicts values of σ_c nearly proportional to μ . Reference 3 also includes results for a hypothetical molecule (μ and α equal to HCl values) with an I_1 value 100 times that of HCl. The results for linear CH_3CN (I_1 value ≈ 40 times HCl) are in agreement with these predictions in that σ_c is nearly independent of the moment of inertia.

CONCLUDING REMARKS

The interpretation of experimental results is complicated by recent experiments reported in reference 7 which indicate that there are competing reaction effects that have been ignored in obtaining ion molecule reaction cross sections. The numerical calculations for symmetric top systems indicate only a slightly stronger dependence of capture cross section on ion energy than calculated for linear polar molecules. It is hoped that these numerical results might serve as a basis for interpreting future experiments on such reactions. However, more reliable absolute values of experimental reaction cross sections are necessary before comparison of theory and experiment can be confidently interpreted in terms of reaction efficiencies.

Lewis Research Center,

National Aeronautics and Space Administration,

Cleveland, Ohio, February 21, 1968,

120-26-03-04-22.

APPENDIX A

EQUATIONS OF MOTION AND VALUES OF MOLECULAR CONSTANTS

The Lagrangian energy expression of reference 1 for the ion-symmetric top molecular system which is depicted in figure 1 is

$$L_T = T - V = \frac{m}{2} (\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2) + \frac{I_1}{2} (\dot{\xi}^2 + \dot{\eta}^2 \sin^2 \xi) + \frac{I_2}{2} (\dot{\psi} + \dot{\eta} \cos \xi)^2$$

$$+ \frac{\mu e}{r^3} \{-X \sin \xi \sin \eta + Y \sin \xi \cos \eta + Z \cos \xi\} + \frac{\alpha e^2}{2r^4} \quad (A1)$$

where m , I , μ , α , and e are the reduced mass, moment of inertia, dipole moment, electronic polarizability, and electronic charge, respectively.

The equations of motion of the system are

$$\frac{d}{dt} \left(\frac{\partial L_T}{\partial \dot{q}} \right) - \left(\frac{\partial L_T}{\partial q} \right) = 0 \quad (A2)$$

where $q = X, Y, Z, \xi, \eta$, and ψ .

For the translational coordinates, equation (A2) reduces to the following equations:

$$\ddot{X} = \frac{\mu e}{mr^5} \{-r^2 \sin \xi \sin \eta - 3XF_v\} - \frac{2\alpha e^2 X}{mr^6} \quad (A3)$$

$$\ddot{Y} = \frac{\mu e}{mr^5} \{r^2 \sin \xi \cos \eta - 3YF_v\} - \frac{2\alpha e^2 Y}{mr^6} \quad (A4)$$

$$\ddot{Z} = \frac{\mu e}{mr^5} \{r^2 \cos \xi - 3ZF_v\} - \frac{2\alpha e^2 Z}{mr^6} \quad (A5)$$

where the potential function

$$F_v = \{-X \sin \xi \sin \eta + Y \sin \xi \cos \eta + Z \cos \xi\}$$

The corresponding rotational coordinate equations are

$$\ddot{\xi} = \dot{\eta}^2 \sin \xi \cos \xi \frac{-\mu e}{I_1 r^3} \{Z \sin \xi - X \cos \xi \sin \eta + Y \cos \xi \cos \eta\} - \frac{I_2}{I_1} (\dot{\psi} \dot{\eta} \sin \xi + \dot{\eta}^2 \sin \xi \cos \xi) \quad (A6)$$

$$\ddot{\eta} = \frac{\left\{ \frac{-\mu e}{r^2} (Y \sin \eta + X \cos \eta) - 2I_1 \dot{\eta} \dot{\xi} \cos \xi + I_2 [\dot{\xi} (\dot{\psi} + \dot{\eta} \cos \xi)] \right\}}{I_1 \sin \xi} \quad (A7)$$

$$\ddot{\psi} = \dot{\eta} \dot{\xi} \sin \xi - \ddot{\eta} \cos \xi \quad (A8)$$

It should be noted that the ion-dipole potential term in equation (A1) has a different form than the term used for the linear polar molecule in reference 3. The dipole moment is assumed to lie along the symmetry axis of the top but the angle η is equal to the conventional azimuthal angle plus $\pi/2$ (see fig. 2). This angle η locates the intersection of the plane normal to the symmetry axis in the x-y plane and not the projection of the symmetry axis in that plane. The form of the interaction potential term changes under the coordinate transformation (to the second Euler system), which was described in Details of the Calculation.

APPENDIX B

VARIABLE STEP-SIZE ROUTINE

There are two general classes of formulas for numerical integration of ordinary differential equations: the multistep (e. g. , predictor-corrector) and the single step or Runge-Kutta. Both types are discussed in reference 8. Multistep formulas are appealing because they yield a higher order of accuracy for the same number of evaluations of the differential equations. However, the Runge-Kutta formulas are more flexible in that they permit step-by-step adjustment of the integration interval. This adjustment feature is especially useful in a system where a reliable, independent indicator of integration error is available. For a conservative interaction the deviation in total energy from its initial value serves as such a check because it can be easily calculated at the conclusion of each integration step. For this reason, Runge-Kutta formulas were used throughout the calculation. The error control and integration interval selection scheme used is essentially empirical; it works well, although it is without a rigorous mathematical basis. The error is considered through R_t , the ratio of the current total energy (at time t) to the initial energy of the system. The error E_t to be tolerated in any step is simply the absolute value of the change in R_t during the step. A value E_T of the total error ($10^{-4} \leq E_T \leq 10^{-2}$) to be tolerated over the total estimated trajectory time T is selected. It is then assumed that the error accumulates monotonically, that is, no cancellation of error. The acceptable error for one integration step of length h at time t (with current energy ratio R_t) is

$$E_t = h \frac{(E_T - |R_t - 1.00 \dots|)}{(T - t)} \quad (B1)$$

If the energy ratio at the end of this step is R'_t , then the actual error accrued during this step is

$$E_a = |R'_t - R_t| \quad (B2)$$

If $E_a > c_1 E_t$, where $1.0 < c_1 \leq 4.0$, then the step is not accepted.

After both successful and unsuccessful steps, one must determine the size h' of the next step. If the step is unsuccessful, the step should be repeated with $h' < h$; and if the step is successful, the next step should be performed with $h' \geq h$. For a Runge-Kutta formula of order m applied to the single differential equation,

$$y' = f(t, y) \quad (B3)$$

the truncation error is given by

$$E_m = Ah^{m+1} + O(h^{m+2}) \quad (B4)$$

where A is a function of the formula used and of $f(t, y)$.

Assuming that $E_a = Ah^{m+1}$ (not theoretically justified), then the value of A can be estimated. With A known, the assumption

$$E'_t = Ah'^{m+1} \simeq \frac{E_a}{h^{m+1}} h'^{m+1} \quad (B5)$$

where E'_t represents the error to be accepted in the next step, yields

$$h' = \frac{E'_t}{E_a}^{1/(m+1)} \cdot h \quad (B6)$$

A limitation on h' which has proved useful and, in fact, necessary for $E_a = 0$, is

$$h' < c_2 h \quad (B7)$$

where $2.0 \leq c_2 \leq 10.0$. In addition, any case is terminated if $h' < 10^{-20}$ seconds. This situation is rarely encountered if realistic values of E_T and T have been assigned.

This procedure for selecting integration intervals satisfies the previously stated qualitative criteria. If an unrealistic estimate is given for the initial step, the step size settles down to a sensible value after two or three integrations (or failures, if the estimate is too large). The scheme has yielded more accurate results and significantly shorter computer run times than fixed-step size routines. Calculations were carried out using Runge-Kutta formulas of order 2 (requiring 2 evaluations of the differential equations per step) and 3 (3 evaluations) both described in reference 9. Calculations were mainly done with orders 4 (4 evaluations - the classic Runge-Kutta method) and 5 (6 evaluations) which are described in references 8 and 10, respectively. Formulas for orders 6 (7 evaluations), 7 (9 evaluations) and 8 (12 evaluations) are described in references 11 and 12.

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